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Study on annealing of infrared nonlinear optical crystal $ZnGeP_2$

Zhenyou Wang [a,b], Mingsheng Mao [a], Haixin Wu [a,*], Youbao Ni [a], Changbao Huang [a,b], Xudong Cheng [a,b]

[a] Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China
[b] Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

$ZnGeP_2$ crystal is one of the most promising materials for infrared nonlinear optical applications. However, the near-band-edge absorption of native defects degrades the performance of ZGP-OPO device. The single-zone-annealing furnaces were utilized to anneal ZGP samples. The optimal annealing temperature was 600 °C and the optimal annealing atmosphere was ZGP powder vapor. For further annealing effects, the two-zone-annealing method was adopted to anneal ZGP crystals for the first time. The absorption coefficient can be reduced to 0.06 cm^{-1} at 2 μm and the resistivity can be increased from $5.8 \times 10^7\ \Omega$ cm to $4.1 \times 10^9\ \Omega$ cm. The results indicate that the annealed $ZnGeP_2$ crystals could be used as OPO devices. The mechanism of the two-zone-annealing effects has been briefly discussed in this paper.

1. Introduction

The $ZnGeP_2$ (ZGP) crystal is known as one of the most promising materials for nonlinear optical applications [1]. Bridgman [2,3] and gradient freeze (GF) [4] techniques are two efficient ways to grow ZGP single crystals to date. However, crystals grown by both methods have native defects absorption which ranges from short-wavelength side of the transparency window to 2.5 μm. This deeply degrades high-power operation when using a 2 μm pump.

The absorption mechanism is dependent upon the crystal stoichiometry and the growth technique. Many studies on the near-infrared absorption have been performed to understand its origin. The defects that result in such absorption in ZGP crystals are probably the zinc vacancy V_{Zn}^{-}, the phosphorus vacancy V_{P}^{0}, as well as of group IV anti-site Ge_{Zn}^{+} [5–7]. Post thermal annealing experiments have been carried out by several research groups to reduce the near-band-edge absorption [8–14]. But some of their results are not consistent with others'. In this paper, we attempt to ascertain the optimal annealing condition (temperature, atmosphere, etc.) by the conventional single-zone-annealing method. For further annealing effects, the two-zone-annealing method was utilized to anneal ZGP crystals with ZGP powder as the annealing source. This is, to our knowledge, the first time to anneal ZGP crystals via such method.

2. Experiments

$ZnGeP_2$ polycrystalline charges were synthesized from stoichiometric amounts of high purity (6N) Zn, Ge, and red P by two temperature-zones vapor transportation method. The single crystals were grown by the vertical gradient freeze method [15]. At the bottom of the crucible, a [001] single crystal was put into its seed pocket. Then the synthesized polycrystalline materials with the excess of 0.1% P-rich were loaded into the crucible which was evacuated at room temperature and sealed under 10^{-3} Pa. The upper region of furnace temperature is 1050 °C and the lower region temperature is 980–1000 °C. The temperature gradient of the growth region is about 2–5 °C/cm. Both furnace zones were lowered at rate of 1 °C/h to grow single crystals. After the melt were completely solidified, the grown crystals were cooled at 5 °C/h through 950 °C and 30 °C/h to room temperature.

Twenty samples sized $5.5 \times 4 \times 2$ mm^3 were cut from one grown ZGP crystal ingot for thermal annealing experiments. The [001] axis was normal to the polished surfaces of samples. A photograph of samples is shown in Fig. 1. The ZGP sample, together with the excess of Zn or ZGP powder, was placed into a quartz crucible which was evacuated at room temperature and sealed under 10^{-3} Pa. Then the crucible was loaded in a single-zone-annealing furnace.

Other samples were annealed by the two-zone-annealing method. The Schematic diagram of the two-zone-annealing furnace and its temperature profile are shown in Fig. 2. The ZGP samples were placed in one end of the crucible, and the boat filled with ZGP polycrystalline powder was put in the other end.

* Corresponding author. Tel./fax: +86 551 5591504.
E-mail address: hxwu@ircrystal.com (H. Wu).

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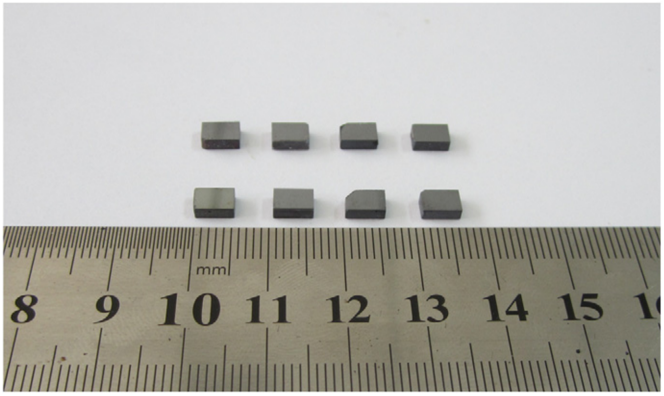

Fig. 1. The photograph of ZGP samples ($5.5 \times 4 \times 2$ mm^3).

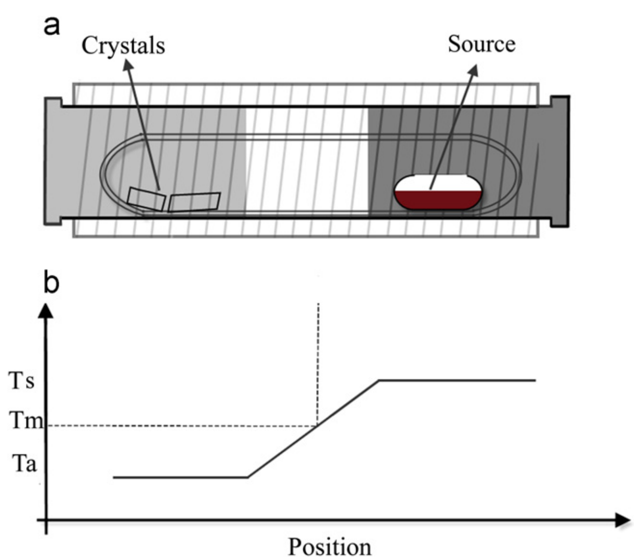

Fig. 2. The Schematic diagram of two-zone-annealing furnace and its temperature profile. T_a: annealing-zone temperature; T_m: the middle of gradient zone temperature; T_s: source-zone temperature.

The crucible was evacuated to 10^{-3} Pa and sealed. Then the crucible was put into the furnace. By adjusting the position of the crucible, the samples should be placed in the annealing-zone (low temperature), and the annealing source should be placed in the source-zone (high temperature).

The transmission spectra of crystals (before and after annealing) were recorded by a lambda 950 UV/Vis/NIR spectrophotometer with wavelength ranging from 0.7 μm to 2.4 μm and the incident light was unpolarized. The resistivity was measured by super-high resistivity instrument EST121 (100 V, DC) at room temperature.

3. Results and discussion

3.1. Single-zone-annealing

The transmission spectrum of polished ZGP samples was measured before annealing, and they were generally identical to one another. Three samples ISA01, ISA02, ISA03, were annealed in Vacuum, Zn and $ZnGeP_2$ powder respectively. Both the annealing temperature (600 °C) and the annealing time (300 h) were kept constant for the three samples.

The absorption coefficients of ZGP samples at 2 μm in different annealing vapor atmospheres were summarized in Table 1. The

Table 1
2 μm absorption and resistivity of single-zone-annealing of ZGP samples.

Sample[a]	Annealing condition	2 μm absorption coefficient (cm^{-1})	Resistivity (Ω cm)
ISA01	600 °C, Vacuum	0.38	4.2×10^8
ISA02	600 °C, Zn	0.43	5.3×10^8
ISA03	600 °C, ZGP powder	0.12	9.5×10^8
ISA07	550 °C, ZGP powder	0.19	6.8×10^8
ISA08	650 °C, ZGP powder	0.37	5.5×10^8

[a] As-grown crystals 2 μm absorption coefficient: 0.47 cm^{-1}; Resistivity: 5.8×10^7 Ω cm; Annealing time: 300 h.

optical absorption coefficient was calculated utilizing the following expression [16]:

$$\alpha = -\frac{1}{L}\ln\left(\left\{\left[\frac{(1-R)^2}{2TR^2}\right]^2+\frac{1}{R^2}\right\}^{1/2}-\frac{(1-R)^2}{2TR^2}\right) \quad (1)$$

where L is the thickness of the sample, T is the transmission, and $R=(n-1)^2/(n+1)^2$ is the Fresnel power reflection coefficient. The refractive indices for the various wavelengths were derived from Kato's Sellmeier equation [17]. The largest reduction of absorption coefficients at 2 μm has been obtained when annealing in ZGP powder. By comparison, the absorption coefficients of ZGP annealed in vacuum and Zn have been reduced slightly. To verify the optimal annealing temperature, ISA07 and ISA08 were annealed in the presence of ZGP powder at 550 and 650 °C respectively. The effects of the annealing temperature on the 2 μm absorption were also listed in Table 1. The results indicated that the optimal annealing temperature was 600 °C. A higher (650 °C) or a lower (550 °C) annealing temperature yielded a smaller reduction of the absorption coefficient at 2 μm.

We have noticed that our results on absorption (depending on annealing atmosphere) differ from results given in paper [8]. But the conclusion that the ZGP powder is the optimal annealing atmosphere agrees with the results reported in paper [11,12]. To some extent, the optimal annealing condition depends on the technology of crystal growth and the initial stoichiometry of crystals. That would be the reason why some researchers' results are different from others' [8–14]. Further studies should be focused on the mechanism of annealing ZGP crystal.

3.2. Two-zone-annealing

On the basis of the single-zone-annealing results, ZGP crystals were annealed by the two-zone-annealing method in the presence of ZGP powder. The samples and the source were arranged in the annealing-zone and the source-zone of the two-zone-annealing furnace respectively. The annealing-zone temperature was fixed to 600 °C and the source-zone temperature was set at 650 °C, 700 °C, 750 °C and 800 °C. The 2 μm absorption coefficient and the resistivity of samples were given in Table 2. The absorption coefficient spectra of as-grown, single-zone annealed and two-zone annealed samples were shown in Fig. 3. From Table 2, We can see that the lowest absorption coefficient was acquired with the source-zone temperature 750 °C. The absorption coefficient decreased by 87% at 2 μm which was much better than the effects of single-zone-annealing in ZGP powder at 600 °C. Additionally, the curves in Fig. 3 show that the optical absorption is overally improved from 0.7 μm to 2.4 μm. Some other ZGP samples including ZGP-OPO devices were annealed in the same conditions. There is more than 80% of the number of two temperature-zone annealed samples whose absorption coefficient is lower than 0.08 cm^{-1} at 2 μm, and the lowest absorption

Table 2
2 μm absorption and resistivity of two-zone-annealing of ZGP samples.

Sample[a]	Source-zone temperature (°C)	2 μm absorption coefficient (cm^{-1})	Resistivity (Ω cm)
TTA01	650	0.18	8.2×10^8
TTA02	700	0.13	1.3×10^9
TTA03	750	0.06	4.1×10^9
TTA04	800	0.31	4.7×10^8

[a] Annealing-zone temperature: 600 °C; Source: ZGP powder; Annealing time: 300 h.

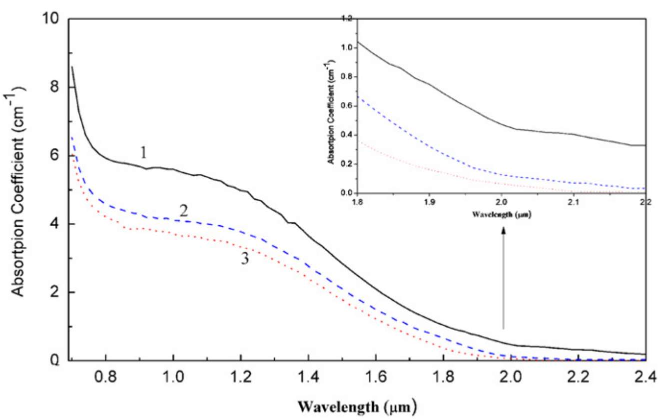

Fig. 3. The absorption coefficient spectra of ZGP Samples from 0.7–2.4 μm: as-grown (curve 1), single-zone annealed (curve 2, 600 °C, ZGP powder), and two temperature-zones annealed (curve 3, 600 °C,750 °C, ZGP powder). For clarity, the other absorption coefficient spectra have not been shown in the figure.

coefficient could be reduced to 0.06 cm^{-1}. Generally, the intensity of absorption is proportional to the concentration of defects. The carrier concentration in the *p*-ZGP crystal is determined by the number of ionized acceptors at room temperature. The carrier concentration *p* can be determined from the following formula:

$$V_H = \left(\frac{1}{pe}\right)\frac{BI}{d} \quad (2)$$

where V_H is the Hall voltage, *e* is the electron charge, *B* is the field, *I* is the current, and *d* is the sample thickness. However, it is hard to acquire the carrier concentration in ZGP crystals using a Hall Effect Measurement System. Because the resistivity of ZGP is too high ($>10^7$ Ω cm). So the resistivity becomes an important parameter to characterize its electronic property. The resistivity of ZGP samples (before and after annealing) has been measured using super-high resistivity instrument. The results were shown in Tables 1 and 2, which indicated that the 2 μm absorption closely connected with the resistivity. The ZGP crystals with higher resistivity mean that they have lower 2 μm absorption. The resistivity of *p*-type semiconductors can be expressed by the formula:

$$\rho = \frac{1}{peu} \quad (3)$$

generally, the Hall mobility of the holes *u* verifies little. The reduction of concentration of the holes *p* is the reason of the increase of the resistivity. So the near-band-edge absorption is directly in connection with the acceptors in *p*-ZGP crystal.

The studies of defects in ZGP crystals by means of EPR and photo-induced EPR indicated that the intrinsic defects are V_{Zn}^{-}, V_P^0 and Ge_{Zn}^{+}. Both the absorption spectra and photo-induced absorption spectra studies in [5–7] and the computer simulation using the pseudo-potential method reached the conclusion that the absorption nearby 2 μm is mainly contributed by Zinc vacancy absorption [18]. Our annealing results also agree with such a conclusion. However, it is difficult to reach an ideal result by simply annealing ZGP crystals in the single-zone-annealing furnace with excess of Zinc. With reference to [19], the concentration of $Ge_{zn}+$, V_{zn}^{-} would be decreased by annealing in Zn vapor. Meanwhile, the concentration of V_P^0 would be increased. The annealing results also indicate that ZGP powder vapor, rather than Zn vapor, is the better annealing atmosphere. The ZGP crystals and the source were separated in two-zone-annealing experiment, which could avoid the second volatilization of the crystals. Additionally, the volatile component of crystals could be appropriately compensated by using ZGP powder as the source. The two-zone-annealing experiment could compensated the deviation of the violate components which evaporated during the ZGP crystal growth from melt. Similarly, the 2 μm absorption was disappeared when the ZGP crystals were grown by the high-pressure vapor transport (HPVT) method [20]. By modifying the source-zone temperature of the furnace, the ideal annealing effects could be obtained.

4. Conclusions

In this study, the ZGP sample has been annealed in the single-zone-annealing furnace to ascertain its optimal annealing temperature and atmosphere. The results indicated that the optimal annealing condition was in the presence of ZGP powder at 600 °C. The two-zone-annealing experiments have been carried out for further annealing effect. The best annealing effect has been acquired when using ZGP powder as the annealing source. The annealing-zone temperature was 600 °C, and the source-zone temperature was 750 °C. The absorption coefficient at 2 μm was reduced to 0.06 cm^{-1} and the resistivity was increased to nearly two orders of magnitude of as-grown ones'. The results indicate that the annealed crystals could be used as OPO devices. The two temperature-zones annealing method could also be applied to anneal other volatile compounds to improve their optical and electrical properties.

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